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A STRONG, SOLID PLASTIC-BASED COMPOSITE MATERIAL AND A METHOD
FOR ITS MANUFACTURE ;

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ABSTRACT:

The invention relates to a composite material comprising an anisotropic, thermotropic liquid-crystalline polymer matrix and/or a mixture of liquid-crystalline polymer(s) and thermoplastic polymer reinforced with carbon fibres.

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| (21) International Application Number: PCT/FI94/00229 (22) International Filing Date: 2 June 1994 (02.06.94) (30) Priority Data: 932549 4 June 1993 (04.06.93) FI (71)(72) Applicants and Inventors: SUOKAS, Esa [FI/FI]; Nikinkatu 25 C 6, FIN-33580 Tampere (FI). TÖRMÄLÄ, Pertti [FI/FI]; Nestori Sarrin katu 1, FIN-33720 Tampere (FI). PELTONEN, Petri [FI/FI]; Katraankatu 3 D 67, FIN-33310 Tampere (FI). (74) Agents: HAKOLA, Unto et al.; Tampereen Patenttitoimisto Oy, Kanslerinkatu 6, FIN-33720 Tampere (FI). | | (81) Designated States: AU, CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> |
| (54) Title: A STRONG, SOLID PLASTIC-BASED COMPOSITE MATERIAL AND A METHOD FOR ITS MANUFACTURE | | |
| (57) Abstract The invention relates to a composite material comprising an anisotropic, thermotropic liquid-crystalline polymer matrix and/or a mixture of liquid-crystalline polymer(s) and thermoplastic polymer reinforced with carbon fibres. | | |

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A strong, solid plastic-based composite material and a method for its manufacture

5 The invention is related to a composite material comprising an anisotropic, thermotropic liquid-crystalline polymer matrix and/or a mixture of liquid-crystalline polymer(s) and thermoplastic polymer reinforced with fibrous reinforcing units.

10

Liquid-crystalline polymers comprise of stiff linear or helical molecular chains. Their main components are aromatic ring structures, which usually are coupled together by ester, ether or amide bonds. Because liquid-crystalline polymers have typically linear molecular chains, their enthalpy is very small. If additionally the internal secondary chemical bonds between polymer chains are strong, like in the case of amides, the polymer cannot be melted by thermal energy. Such polymers can be processed only after dissolving to a suitable solution. Such liquid-crystalline polymers are called lyotropic. To these polymers belong e.g. commercial aromatic parapolyamides, like poly-1,4-phenylene terephthalic amide (trade mark Kevlar of DuPont). This was the first technical liquid-crystalline polymer, which was launched in the middle of 70's.

25

Another main group of liquid-crystalline polymers (or plastics) comprise thermotropic polymers. They can be processed by means of heat and pressure (or with the traditional processing methods of the thermoplastics), because their internal secondary chemical bonds have been diminished by molecular modifications. Accordingly these polymers can be processed with melt spinning, extrusion or injection molding. Thermotropic liquid-crystalline polymer melts show local microscopical unisotropy of the structure, which structure can be

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shifted to the unisotropy of the macrostructure by means of processing.

5 Thermotropic liquid-crystalline polymers (LC polymers) are a broad group of materials, where different properties differ significantly from each other in the case of different polymers.

10 LC polymers can be divided to three groups on the basis of their heat-deflection temperature. The first group includes polymers which crystallize almost completely. Therefore their heat resistance is almost as good as with thermoplastic polyimides. Commercial Xydar (Amoco Premark) which is made of p,p'-bisfenol, 15 p-hydroxybenzoic- and terephthalic acid belongs to this group.

20 The strength and the stiffness of LC polymers of the first group are high because of the linear structure of the molecular chains. These thermotropic polymers can be processed with traditional melt molding methods, e.g. with injection molding. Because of the liquid-crystalline behaviour the melt viscosity of Xydar is above 1000 Pas at temperature = 430°C and at shear 25 speed of 1000 s⁻¹. Because the LC-transition of this type of thermotropic polymers happens at high temperatures (e.g. for Xydar SRT-300 at 421°C), they must be processed with modified extruders and injection molding machines.

30 The LC-transition point of the liquid-crystalline polymer diminishes, if the polymer is synthesized of monomers which have crankshaft conformations which prevent the tight packaging of polymer chains (preventing also the development of crystallinity). These 35 thermotropic polymers are typical semi-crystalline thermoplastics, but in the amorphous glass state their molecules are not oriented randomly, but uni-

axially or nematically. These are polymers belonging to the second group of thermotropic polymers when classified according to their thermal strength. The thermal strength of these polymers is not determined by their LC-transition. The heat deflection temperature of this type of polymers is usually nearer to the LC- than glass transition. The best known commercial polymer of this group is p-hydroxybenzoic- and 6-hydroxy-2-naphtoic acid polymer Vectra A900 (Hoechst Celanese). Vectra A900 has the LLC-transition at 280°C, the heat deflection temperature 180°C (1.82 MPa) and a typical crystallinity of 20 %. The melt viscosity of Vectra A900 is 60 Pas at 300°C and at shear speed of 1000 s⁻¹.

The third group of thermotropic polymers comprises molecules where the processability has been made better by adding flexible units, like a methylene chain, to the stiff molecule. In this case the crystallinity and heat deflection temperature decreases, but the toughness increases. The commercial example is p-acetoxybenzoic acid/polyethylene terephthalate polymer F7-G (Eastman). Its viscosity is ca. 10 Pas at temperature 260°C and at shear speed 1000 s⁻¹.

A typical processing method for plastics is injection molding. This process can be divided to the following steps: plasticization, injection, after-pressure step and removal of the product.

The polymer melt which has been plasticized with the screw, is injected into a relatively cold mold cavity, which is filled rapidly. In the injection step the pressure is very high. Thereafter the after-pressure forces more plastic into the mold and finally the product is cooled and removed at the same time when the machine plasticizes a new portion of polymer melt.

During the mold-filling step the sophisticated movement of the polymer melt can be divided into three parts:

- shear flow, which is seen in the cylindrical parts (e.g. in tubes),
- 5 - tapering or stretching flow, which is seen when the broad cross-section is reducing,
- expanding flow, which is caused by the increasing of the cross-sectional area.

10 Shear-deformation is dominant in injection molding. It tries to revolve both flexible and especially stiff molecules. Shear deformation is most effective, when the temperature gradient is big. Stretching deformation elongates flexible molecules or stiff
15 molecule groups, which makes uni-axial orientation stronger in the direction of the deformation. Stretching deformation dominates melt-spinning. The best mechanical properties for polymers are received with uni-dimensional structures, where the cross-sectional
20 area is small. This can be seen clearly when making fibres and films. In the expanding flow the uni-axial stress slows down the speed of the melt and the molecules try to orientate in the transverse direction against the movement vector.

25 Thermotropic LC-polymers comprise of stiff molecules, which orientate easily in the shearing and stretching flow. In conventional injection molding steps the surface orientation of liquid-crystalline polymer
30 melt is axial and the internal orientation radial. Similar surface/core morphology has been seen in connection with fibre-reinforced plastics. In thermotropic liquid-crystalline polymer samples manufactured by injection molding the number of oriented layers
35 can be even 7-9.

The microstructural heterogeneity of the injection molded thermotropic LC-polymer and the orientation

gradient in the direction of the thickness of the sample reduce significantly the mechanical properties of the final product. In this invention we describe a composite material and a method to manufacture it, where the effects of the disadvantageous variations of the molecular orientation (originating from the flow of the unisotropic melt) in the surface/core-micro-structure of the final product to its mechanical properties have been eliminated. The invention describes a composite sample, where the solid, compact structure gives the material excellent mechanical properties.

In the invention we combined with each other the fibrous matrix and the reinforcing material. The matrix can be whatever thermotropic LC-polymer, mixture of two or several LC-polymers or a mixture of LC-polymer with a thermoplastic polymer (like PET). The matrix material can be also in the melt state so that it can be combined with the reinforcing fibres with cross-head extrusion or with pultrusion melt impregnation. The reinforcing materials can be continuous mono- or multifilament, glass fibre, plastic fibre (e.g. polyester), metal fibre or ceramic fibre, but the most advantageous embodiment according to the characteristic part of claim 1 is continuous carbon fibre. The matrix and/or reinforcing materials can be combined with each other initially in proper relation as hybriide fibres, threads, filaments, fabrics, cords, knits or as some other corresponding prepreg material. The matrix material and the reinforcing fibres are combined to each other either with a batch process like compression molding, or with a continuous process like with pultrusion or filament winding.

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In compression molding the matrix and the reinforcing fibres are laminated into the mold cavity, where they are compressed with temperature and pressure to a

sample. It is very important to control the temperature and the pressure carefully. The temperature control can be done e.g. with a thermoprobe and the pressure can be measured with a pressure meter. The best properties of the final product can be received using the following time-temperature-pressure profile:

- phase 1: heating to the first holding temperature (T_{h1} as a variable)
- phase 2: thermal treatment in the first holding temperature (t_{h1} as a variable)
- phase 3: increasing of the temperature to the second holding temperature (T_{h2} as a variable)
- phase 4: thermal treatment in the second holding temperature (t_{h2} as a variable)
- phase 5: increasing of the temperature to the third holding temperature (T_{h3} as a variable)
- phase 6: thermal treatment in the third holding temperature (t_{h3} as a variable)
- phase 7: reduction of the temperature to the tightening temperature (T_c as a variable)
- phase 8: thermal treatment in the tightening temperature (t_c as a variable) using a determined pressure (p_c as a variable)
- phase 9: cooling to the removing temperature (T_r as a variable)
- phase 10: removal of the final sample.

The three-stage heating profile secures the shift of the heat into the interior of the unisotropic matrix/reinforcing fibre sample. When the matrix material is thermotropic liquid-crystalline polymer, the highest or the third holding temperature (T_{h3}) must be adjusted to the nearness of the LC-transition point of the nematic LC-polymer. The tightening temperature (T_c) can be the same as the third holding temperature (T_{h3}), but the best result is obtained when the

compression temperature (T_C) is smaller than the first holding temperature (T_{H1}).

5 The most advantageous material combination of the invention comprises thermotropic LC-polymer and carbon fibres, whose relative amounts can be varied between 0-100 %. The best mechanical properties are obtained by using the pre-pressure profile given in Figure 2. The detailed description of the method is given in
10 Examples 1-3. Essential in the method of the invention is that pre-pressure p_0 is directed into the sample already in the room temperature 23°C. When the heating of the sample is started, the pre-pressure p_0 remains constant up to the temperature which corresponds some
15 thermal transition (like the glass transition T_g) of the matrix material. Thereafter the pre-pressure p_0 approaches the value 0. The pre-pressure p_0 causes the flow of the matrix material both axially and radially in relation to the reinforcing phase. This
20 helps the combination of the components by means of wetting or impregnation. The unisotropical flow behaviour of thermotropic LC-polymer facilitates the wetting. During the final tightening molding period the matrix/reinforcement combination is pressurized
25 with the final pressure p_C , which affects up to the removal of the final sample.

The parameter profile of the batch process (compression molding) can be modified to a continuous method, like
30 melt impregnation and pultrusion. In these methods the matrix and the reinforcing fibres are mixed better and the volume fraction of the reinforcing fibres can be increased significantly. The application of continuous manufacturing methods makes advantageously
35 possible the use of prepreg-samples where the matrix and the reinforcing fibres have been combined to uni-axial, but also to bi- or three-dimensional forms, like fabric, velour, cord, laminate or some correspond-

ing form. Such semi-finished products can be treated continuously in pultrusion or filament winding.

5 The excellent transverse mechanical properties of the material of the invention can be obtained only by using the pre-pressure, which is seen from the Figures 3 and 4. Additionally the matrix and the reinforcing fibre materials must be compatible to give a sample of the invention having a strong solid structure. This is manifested e.g. as the hardness of the surface and as a glassy gloss. Evidently the pre-pressure makes adhesion between the thermotropic LC-polymer and carbon fibres better which is seen as good mechanical properties of the material. The molecular interpretation of the improvement of the adhesion may be the increasing of the functional polar group on the surface of the carbon fibres as a consequence of oxidation. Another explanation could be the transcrystallization of LC-polymer on the surface of the carbon fibres.

20 The longitudinal mechanical properties of the composite material of the invention are determined by means of the reinforcing fibres, because the final sample is typically uni-axial. Advantageously the material of the invention is a composite of thermotropic LC-polymer and carbon fibres, which material is also electrically conductive. This type of material can be characterized as a semiconductor. Accordingly in the material of the invention excellent mechanical properties and partial electrical conductivity are combined. This material combination is extremely potential in applications of electronics-, aviation- and space industrial applications.

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The material of the invention can be also coated with a plastic layer which acts as an electrically isolating layer giving the material, whose interior is elec-

(p_c). Because of the small flow viscosity of the LC-melt, the wetting of the carbon fibres was efficient. After the impregnation combined with the tightening molding, the mold was cooled below the glass transition of the used LC-polymer ($T_g = 100^\circ\text{C}$). Finally the sample was removed from the mold.

Figure 2 shows the used pressure profile of the compression molding. Because of the pre-pressure (p_0) the carbon fibres are wetted efficiently. The increasing of the adhesion between the LC-polymer matrix and the carbon fibres can be seen as the increase of bending strength and -modulus of the composite from Figure 3 and 4.

Example 2.

Composite sample was manufactured by combining the commercial liquid-crystalline polymer fibres Vectran M (Hoechst Celanese) and commercial carbon fibres Grafil HS 33-500 12 K (Grafil Inc., Carbon Fibres) to each other by the weaving technique. The fabric structure was simple linen and the fabric was made into the form of a tube. The LC-polymer fibres were used as weft and the carbon fibres as warp. Otherwise the working was done like in Example 1. With the volume fraction 55 % of carbon fibres the following properties for the composite were obtained:

- bending strength: 473 MPa
- bending modulus: 59 GPa.

Example 3.

The composite sample was manufactured with the melt impregnation technique by melting the commercial

trically conductive or semiconductive, an outer surface of an electrical isolator.

5 The invention will be described more closely with reference to the accompanying examples and drawings, in which

10 Fig. 1 illustrates compression moulding of the composite structure in cross-sectional side view,

Fig. 2 shows the moulding pressure profile of the stage of compression moulding of the composite structure,

15 Fig. 3 shows the flexural strength of the composite structure according to an advantageous embodiment as a function of pre-pressure, and

20 Fig. 4 shows the flexural modulus of the composite structure according to another advantageous embodiment as a function of pre-pressure.

25 EXAMPLES

Example 1.

30 Hybride fibre techniques were used to combine commercial LC-polymer fibres Vectran M (Hoechst Celanese) with commercial carbon fibres Besfight HTA W1000 1K (Toho). The fibres were wound to fill the cavity of a compression mold. The unnecessary material was cut off. The mold was closed and the temperature of the
35 mold was increased to the melting point of the LC-fibres, above 280°C. The LC-polymer fibres melted and formed an unisotropic matrix. The LC-melt wetted the carbon fibres because of the compression pressure

liquid-crystalline polymer Vectra A950 (Hoechst Celanese) in a single screw extruder and by combining the LC-polymer melt in a cross-head die with the commercial carbon fibre Grafil HS 33-500 (Garfil Inc., Carbon Fibres). By using inside of the die pegs which spread the carbon fibre bundle, the unisotropic polymer melt wetted the carbon fibres. The LC-polymer wetted carbon fibre bundle was formed in the exit part of the die to a band. The continuous prepreg was cut to 10 cm long samples and these were compression molded to composite samples according to Example 1. With the volume fraction of 47 % of carbon fibres the following properties were obtained:

- bending strength: 858 MPa
- bending modulus: 78 GPa.

Claims

1. Composite material, comprising an anisotropic, thermotropic liquid-crystalline polymer matrix and/or a mixture of liquid-crystalline polymer(s) and thermoplastic polymer reinforced with fibrous reinforcing units, characterized in that the reinforcing fibres are continuous carbon fibres.
2. Composite material according to the claim 1 characterized in that the anisotropic matrix polymer or matrix polymer which is blended with another liquid-crystalline polymer or with thermoplastic polymer, is selected from at least one of the following group:
- 1) polyester
 - 2) polyester amide
 - 3) polyether
 - 4) polyamide.
3. Composite material according to claims 1-2, characterized in that the LC-polymer matrix is blended with another thermoplastic polymer, like polysulphone, polyetherether ketone, polyether ketone, polyether imine or polyether amide.
4. Composite material according to claims 1-3, characterized in that the volume of the reinforcing carbon fibres in the composite is between 1-99 volume %.
5. Composite material according to claims 1-4, characterized in that the liquid-crystalline polymer matrix and the reinforcing continuous carbon fibres are combined to each other with the hybride fibre techniques.
6. Composite material according to claims 1-5, characterized in that the liquid-crystalline polymer

fibres and the reinforcing carbon fibres are combined to each other with the weaving techniques.

5 7. Composite material according to claims 1-6, characterized in that the anisotropic liquid-crystalline polymer matrix and the reinforcing continuous carbon fibres are combined to each other with the melt impregnation techniques in such a way that the LC-polymer melt is combined with carbon fibres in a cross-head impregnation die.

15 8. Composite material according to claims 1-7, characterized in that the LC-polymer matrix and the continuous carbon fibre reinforcement (which is oriented in a controlled way) will be compression molded to a solid sample using temperature and pressure to unite the material components.

20 9. Composite material according to claim 8, characterized in that the matrix LC-polymer and the carbon fibre reinforcement combination are pressurized at room temperature with pre-pressure, which affects during the whole heating cycle of the compression molding in such a way that the unisotropic LC-polymer melt wets the carbon fibres.

30 10. Composite material according to any claim 1-9, characterized in that it is used as raw material to manufacture a hip endoprosthesis or a component of a hip endoprosthesis.

35 11. Composite material according to claims 1-11, characterized in that the carbon fibre reinforced liquid-crystalline polymer composite is coated with a plastic layer which acts as an electrically isolating layer giving the material, whose interior is electrically conductive or semiconductive, an outer surface of an electrical isolator.

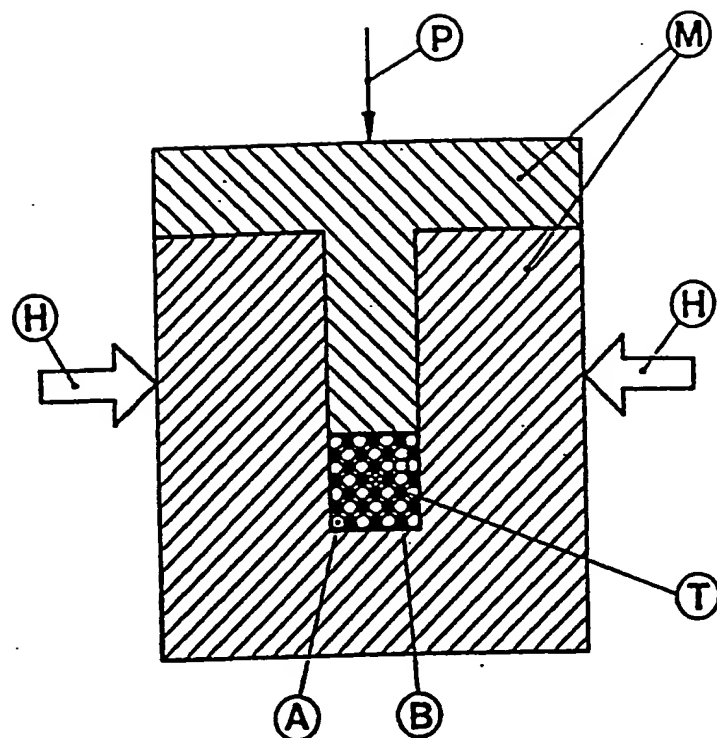


Fig. 1

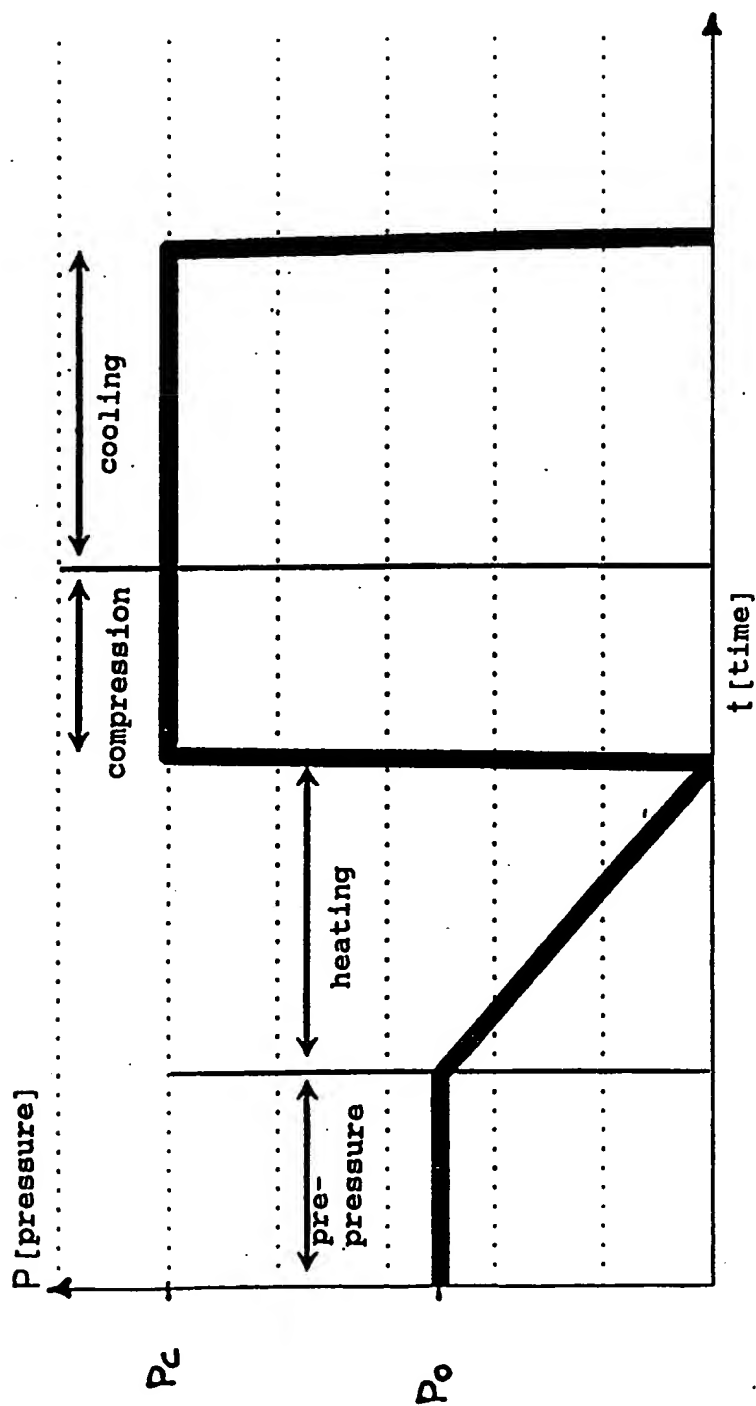


Fig. 2

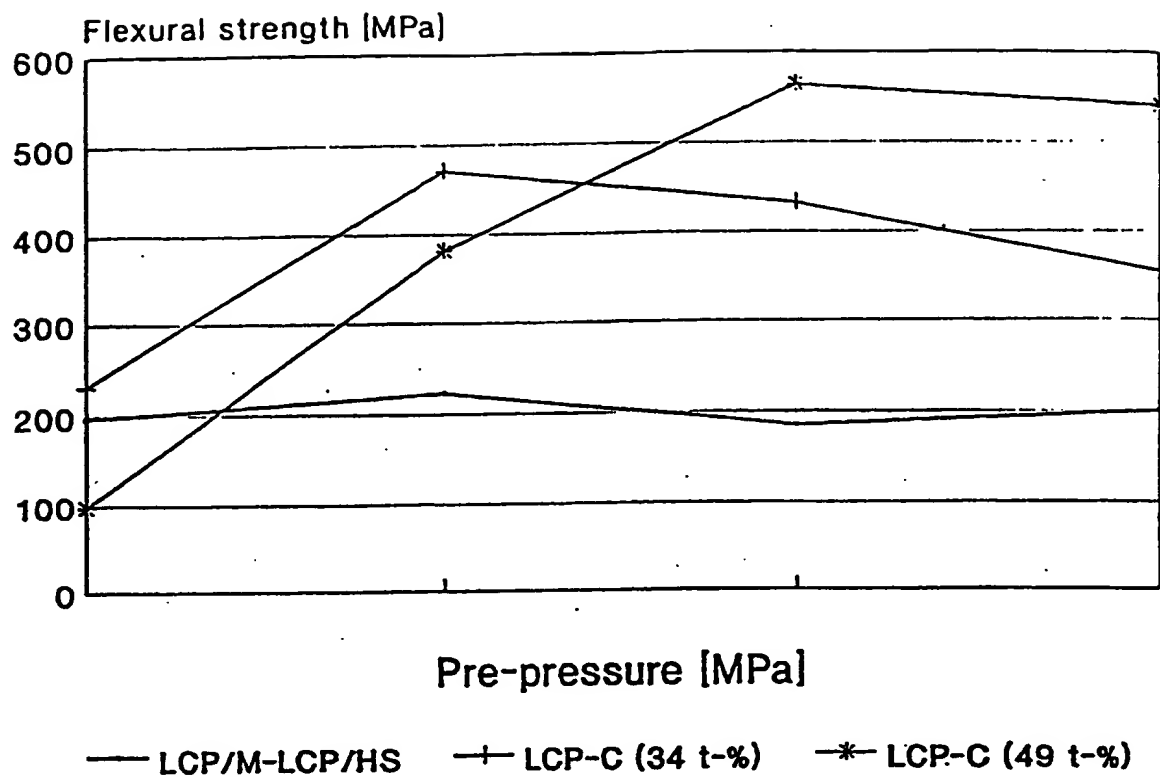


Fig. 3

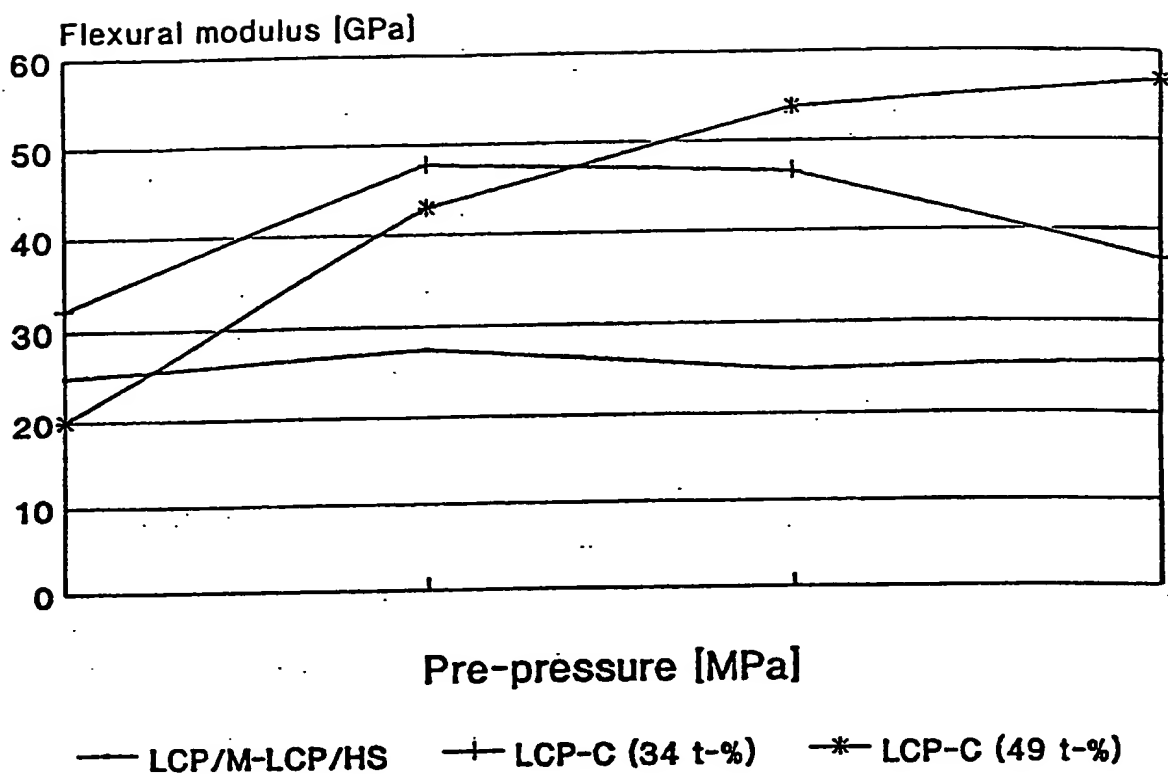


Fig. 4

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C08L 101/00 // C08L

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| X | EP, A2, 0206600 (POLYPLASTICS CO. LTD.), 30 December 1986 (30.12.86), claims 1-4, abstract | 1-11 |
| X | Dialog Information Services, file 351, Derwent WPI, Dialog accession no. 007241711/5, WPI accession no. 87-238718/34, MITSUBISHI RAYON KK: "Carbon fibre-liquid crystalline high polymer intermediate moulding - with high heat resistance and stiffness, useful in aerospace applications", JP 62161528 A 870717 8734 (Basic) | 1-11 |
| X | US, A, 4540737 (KURT F. WISSBRUN ET AL), 9 October 1985 (09.10.85), claims 1, 11-12, abstract | 1-11 |



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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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| A | Patent Abstracts of Japan, Vol 15, No 60, C-805, abstract of JP, A, 2-289651 (UBE IND LTD), 29 November 1990 (29.11.90) -- | 1-11 |
| A | EP, A2, 0499387 (BP AMERICA INC.), 19 August 1992 (19.08.92) ----- | 1-11 |

INTERNATIONAL SEARCH REPORT
Information on patent family members

27/08/94

International application No.
PCT/FI 94/00229

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP-A2- 0206600 | 30/12/86 | JP-B- 1055668 | 27/11/89 |
| | | JP-A- 61285249 | 16/12/86 |
| | | US-A- 4777204 | 11/10/88 |
| US-A- 4540737 | 09/10/85 | EP-A- 0117098 | 29/08/84 |
| EP-A2- 0499387 | 19/08/92 | CA-A- 2060494 | 14/08/92 |
| | | CN-A- 1067913 | 13/01/93 |
| | | JP-A- 5214253 | 24/08/93 |